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54 Method of plasma enhanced silicon oxide deposition.

57 A method of depositing a hard silicon oxide based film is provided by controllably flowing a gas stream including an organosilicon compound into a plasma and depositing a silicon oxide onto a substrate while maintaining a pressure of less than about 100 microns during the depositing. The organosilicon compound is preferably combined with oxygen and helium and at least a portion of the plasma is preferably magnetically confined adjacent to a substrate during the depositing, most preferably by an unbalanced magnetron. These silicon oxide based films may be reproducibly deposited on small or large substrates, such as glass, plastic, mineral or metal, with preselected properties.

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## Description

## METHOD OF PLASMA ENHANCED SILICON OXIDE DEPOSITION

Field of the Invention

5 The present invention relates to the deposition of silicon oxide based films, and more particularly to the plasma enhanced deposition of silicon oxide based thin films from volatile organosilicon compounds.

Background of the Invention

10 Plasma polymerization has been a known technique to form films on various substrates. For example, mixtures of silane with or without oxygen, nitrous oxide or ammonia have been plasma polymerized to form silicon oxide films. However, silane has a repulsive odor, can be irritating to the respiratory tract and is pyrophoric and corrosive.

15 Some attention turned from silane to the deposition of organosilicon films in plasmas. Sharma and Yasuda, Thin Solid Films, 110, pages 171-184 (1983) reviewed the preparation of films from several organosilicon compounds in which silicon based polymers were deposited and described the plasma polymerization of tetramethyldisiloxane by a magnetron glow discharge with the addition of oxygen gas. The films so formed were reduced in carbon to silicon ratio with respect to the organosilicon starting material, but still retained a significant amount of carbon. However, the incorporation of oxygen in the feed mixture, despite silicon enrichment of the film, resulted in poor polymer adhesion.

20 Sacher et al., US Patent No 4,557,946, issued December 10, 1985 describes use of plasma polymerized coatings from organosilicon compounds to form a moisture barrier on the substrate by heating the substrate and controlling the plasma power level. Wertheimer et al., US Patent No 4,599,678, issued July 8, 1986, discloses use of an organosilicon in a glow discharge to coat thin film capacitors when these substrates are heated to a temperature in excess of 50° C.

25 In general, the films formed from organosilicons have typically been formed at a relatively low deposition rate (as compared with, for example, sputtering), have tended to be soft, and often have been hazy. The requirement that the substrate be heated, as in Sacher et al. and Wertheimer et al., is also disadvantageous for some substrates.

In the Drawings

35 Figure 1 is a general schematic diagram illustrating a plasma system utilizing the various aspects of the present invention;

Figure 2 schematically illustrates a side sectional view of the plasma deposition chamber and its associated equipment;

Figures 3A and 3B illustrate the use of a balanced magnetron in the system of Figure 2;

Figures 4A and 4B illustrate the use of an unbalanced magnetron in the system of Figure 2;

40 Figure 5 illustrates an alternative connection to a magnetron in the system of Figure 2 wherein the electric field is produced by a radio frequency generator.

Summary of the Invention

45 It is an object of the invention reproducibly to deposit adherent, hard silicon oxide based, preferably thin films, preferably with preselected properties and preferably at commercially feasible deposition rates.

50 In one aspect of the invention, a method of depositing an adherent, hard silicon oxide based film comprises providing a gas stream with at least three components, establishing a glow discharge plasma derived from the gas stream, or one of its components, in a previously evacuated chamber with a substrate removably positioned in the plasma, and controllably flowing the gas stream into the plasma to deposit a silicon oxide onto the substrate when positioned in the plasma. The gas stream includes a volatilized organosilicon compound, oxygen, and an inert gas such as helium or argon.

55 The gas stream is controllably flowed into the plasma by volatilizing the organosilicon exterior the chamber and admixing metered amounts with oxygen and the inert gas. An unbalanced magnetron preferably confines a portion of the plasma adjacent the substrate during the depositing which increases the ion flux and thus increases the film deposition rate.

60 Films of the invention can be controllably deposited on a variety of large or small substrates for applications in which a hard, protective film, or barrier, is desired. Properties of the films can be selectively modified as appropriate for particular applications.

Detailed Description of the Preferred Embodiments

The present invention provides a method of depositing silicon oxide based films that are hard, adherent and

preferably substantially inorganic. Such films have been deposited in accordance with the invention on a variety of substrates with thicknesses between about 500 Angstroms to about 1 micron, although films thicker than 1 micron can be obtained and are within the scope of the invention.

Choice of the substrate to be coated by the invention will vary according to the desired application. For example, various plastics such as polycarbonate resins, useful for packaging foods or beverages may be coated in accordance with the invention to prevent oxygen or moisture permeation. Thin films in accordance with the invention may be deposited on gallium arsenide semiconductors for insulation and passivation since the substrates are not heated during practice of the invention. Glass or coated glass may be used as substrates for architectural purposes and be coated (or overcoated) in accordance with the invention. Prescription lenses of optical glass or plastic may be coated to protect against abrasion. Other applications include use of the films as orienting layers in liquid crystal displays, as laser light guides in optoelectronic devices, and in various medical applications, such as coating on activated charcoal or other substrates.

Although the process has an organosilicon compound as a starting material, the preferred films are substantially inorganic as evidenced by bonding analysis. However, films that are silicone in nature may be prepared if desired, as further described hereinafter. The typical, substantially inorganic silicon oxide based films deposited in accordance with the invention are characterized by a high degree of crosslinking (determined by Fourier transform infrared spectroscopy, or FTIR).

The inventive method is conducted in a previously evacuated chamber of glow discharge from a gas stream including at least three components: a volatilized organosilicon component, an oxygen component and an inert gas component. The combination of oxygen component and inert gas component with the volatilized organosilicon compound has been found to greatly increase the hardness property of thin films.

As will be exemplified hereinafter, films prepared either with the organosilicon combined only with oxygen or the organosilicon combined only with an inert gas such as helium or argon has a hardness measured by the ASTM D3363-74 (standard test method for film hardness) pencil test of only 2 or 3. By contrast, films made in accordance with the invention have hardnesses by this test of about 7 to about 9+. The numbers reported are based on a scale of 0 to 10 where 0 means the least scratch resistance, while 10 means there was no damage to the coating when abraded in accordance with ASTM D3363-74. Accordingly, thin films prepared in accordance with the invention are harder by a factor of 2 or 3 with respect to films deposited with the volatilized organosilicon component in combination with either oxygen or inert gas.

Suitable organosilicon compounds for the gas stream are liquid at about ambient temperature and when volatilized have a boiling point above about ambient temperature and include methylsilane, dimethylsilane, trimethylsilane, diethylsilane, propylsilane, phenylsilane, hexamethyldisilane, 1,1,2,2-tetramethyl disilane, bis(trimethylsilyl) methane, bis(dimethylsilyl) methane, hexamethyldisiloxane, vinyl trimethoxy silane, vinyl triethoxy silane, ethylmethoxy silane, ethyltrimethoxy silane, divinyltetramethyldisiloxane, divinylhexamethyltrisiloxane, and trivinylpentamethyltrisiloxane.

Among the preferred organosilicons are 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, vinyltrimethylsilane, methyltrimethoxysilane, vinyltrimethoxysilane and hexamethyldisilazane. These preferred organosilicon compounds have boiling points of 71°C, 101°C, 55.5°C, 102°C, 123°C, and 127°C, respectively.

The volatilized organosilicon component is preferably admixed with the oxygen component and the inert gas component before being flowed into the chamber. The quantities of these gases being so admixed are controlled by flow controllers so as to adjustably control the flow rate ratio of the gas stream components.

The organosilicon compound and oxygen of the gas stream during the depositing are preferably in a flow rate ratio between about 1.2:1 to about 1:1.8, and the inert gas of the gas stream preferably is helium or argon, more preferably is helium. When the inert gas in helium or argon, then the preferred flow rate ratio of organosilicon compound, oxygen and inert gas is about 1 to 1.8:1.5 to 1.8 to 2.3.

In addition to the necessary organosilicon, oxygen and inert gas in the gas stream, minor amounts (not greater than about 1:1 with respect to the organosilicon, more preferably about 0.4 to 0.1:1 with respect to the organosilicon) of one or more additional compounds in gaseous form may be included for particular desired properties. For example, inclusion of a lower hydrocarbon such as propylene improves most properties of the deposited films (except for light transmission), and bonding analysis indicates the film to be silicon dioxide in nature. Use of methane or acetylene, however, produces films that are silicone in nature. The inclusion of a minor amount of gaseous nitrogen to the gas stream increases the deposition rate, improves the transmission and reflection optical properties on glass, and varies the index of refraction in response to varied amounts of N<sub>2</sub>. The addition of nitrous oxide to the gas stream increases the deposition rate and improves the optical properties, but tends to decrease the film hardness. A particularly preferred gas stream composition has 20 to 40 SCCM organosilicon, 20 to 40 SCCM O<sub>2</sub>, 40 to 60 SCCM He, 1 to 10 SCCM propylene and 5 to 20 SCCM N<sub>2</sub>.

In practice of the invention method, a glow discharge plasma is established in the previously evacuated chamber. This plasma is derived from one or more of the gas stream components, and preferably is derived from the gas stream itself. The desired substrate is positioned in the plasma, preferably adjacent the confined plasma, and the gas stream is controllably flowed into the plasma. The substrate is preferably conveyed into and out of the plasma adjacent the confined plasma for a sufficient number of passes to obtain the desired film thickness.

The inventive method is preferably practiced at relatively high power and quite low pressure. Thus, for example, most of the films have been prepared at about 1,000 watts (40 kHz), although films have been prepared at 375 (13.56 MHz), and some at 300 watts, direct current. A pressure less than about 100microns

(0.1 Torr) should be maintained during the deposition, and preferably the chamber is at a pressure between about 43 to about 49 microns during the deposition of film.

The substrate is electrically isolated from the system (except for "electrical" contact when in the plasma) and is at a temperature of less than about 80°C during the depositing. That is, the substrate is not deliberately heated.

The flow control is selective for desired film properties, and preferably is by a diagnostics method that includes monitoring a ratio of a hydrogen (alpha) to inert gas emission lines and an electron temperature in the plasma. The general vacuum system in which the inventive method may be practiced and the preferred diagnostics method will now be more fully described.

### General System

Referring initially to Figure 1, a system is schematically illustrated that includes an enclosed reaction chamber 11 in which a plasma is formed and in which a substrate, such as substrate 13, is placed for depositing a thin film of material on it. The substrate 13 can be any vacuum compatible material, such as metal, glass, some plastics and other coated substrates. One or more gases are supplied to the reaction chamber by a gas supply system 15. An electric field is created by a power supply 17, and a low pressure is maintained by a pressure control system 19. An optical emission spectrometer 21 is connected through an optical fiber light transmission medium 23 to the reaction chamber in some appropriate manner to couple the visible and near visible (especially the ultraviolet range) emission of the plasma to the spectrometer. A quartz window 24 in a side wall of the reaction chamber can be used to optically couple the plasma emission with the external fiber medium 23. A general system control 25, including a computer control portion, is connected to each of the other components of the system in a manner to receive status information from them and send controlling commands to them.

The reaction chamber 11 can, in the system of Figure 1, be of an appropriate type to perform any of the plasma-enhanced chemical vapor deposition (PECVD) or plasma polymerization processes. A more detailed explanation of certain components of the system of Figure 1 is given with respect to Figure 2, an example of the PECVD or plasma polymerization process being given. The reaction chamber 11 is divided into a load lock compartment 27 and a process compartment 29 by an isolation gate valve 31. The pressure control system 19 includes a mechanical pump 33 connected to the load lock chamber 27 by a valve 35. The pressure control system also includes diffusion pumps 37 and 39, and an associated mechanical pump 41. The diffusion pump 37 is connected to the load lock chamber 27 through an isolation gate valve 43 and an adjustable baffle 45. Similarly, the diffusion pump 39 is connected to the process chamber 29 through an isolation gate valve 47 and an adjustable baffle 49. The baffle 49 is controlled by the system control 25, while a coating process is being carried out, in order to maintain the internal pressure at a desired value.

A substrate to be coated is first loaded into the load lock compartment 27 with the valve 31 closed. The mechanical pump 33 then reduces the pressure most of the way to the high vacuum region. The diffusion pump 37 is then operated to reduce the pressure further, to about  $5 \times 10^{-6}$  Torr. The operating pressure is typically in the neighborhood of 46 microns for a PECVD or plasma polymerization process and is achieved by flowing the process gases into the reaction chamber and throttling diffusion pump 39 using baffle 49. During loading and unloading operations, the diffusion pump 39 maintains the deposition chamber 29 at the operating pressure. Once the load lock chamber 27 is reduced to base pressure, the valve 31 is opened and the substrate 13 moved into deposition chamber 29.

Provision is made for moving the substrate 13 back and forth through a region 51 where a plasma is formed. In the example system being described, this is accomplished by a plurality of rollers 53, preferably made of aluminium with substrate supporting, electrically insulated O-ring spacers. The rollers or similar material are driven by a motor source (not shown) to rotate about their axes at controllable speeds and thus move the substrate 13. A typical deposition process involves passing the substrate 13 back and forth through the plasma 51 a number of times in order that the thin film deposited on the top of the substrate 13 has a desired uniform thickness.

A magnetron is positioned within the chamber 29, formed of a magnetic structure 55 and a cathode 57. The power supply 17 has its output connected between the cathode 57 and a metallic body of the reaction chamber 29. The magnetron creates an appropriate combination of magnetic and electrical fields in the region 51 in order to create a plasma there when the proper gases are introduced into the reaction chamber 29. The substrate 13 is maintained electrically isolated and is passed directly through the plasma region 51.

The gaseous components necessary for the plasma to form in the region 51 are introduced into the deposition chamber 29 by a conduit 59. A tube (not shown) having plurality of gas supply nozzles along its length is positioned across the width of the chamber 29 (in a direction into the paper of Figure 2) at the position where the conduit 59 enters the chamber. That gas flows within the deposition chamber 29 from the supply tube to the diffusion pump 39, as shown in dotted outline in Figure 2. It has been found preferable to introduce the gas on the side of the plasma region 51 that is closest to the pump 39. A pair of baffles 61 and 63 on either side of the magnetron also helps to confine the gas flow to the plasma region 51.

A particular gas supply system 15 that is connected to the conduit 59 depends, of course, on how many gases are being combined and their nature. In the example of Figure 2, two separate sources 65 and 67 of gases under high pressure are utilized, fewer or additional such gas sources being necessary for other

processes. also, in this particular example, a source 69 of a liquid material to be vaporized is provided. A vaporizing apparatus 71 (that also controls flow) provides the desired flow of vapor into the input conduit 59, in accordance with a control signal from the system control 25. Similarly, the high pressure gases 65 and 67 are delivered through individually controlled flow meters 73 and 75, respectively. An important control of the plasma 51, and thus of the resulting film deposited on the substrate 13, is provided by the ability to adjust the proportions of each gaseous component that is flowing through the inlet tube 59 and into the deposition chamber 29. The flow meter 73 and 75 and vaporizing apparatus 71 each supply the system control 25 with an electrical signal proportional to the flow rate of gas through it, and also responds to a signal from the system control 25 to adjust and control the flow rate.

### Magnetron Structures

The magnetron used in the plasma chamber 29 can be of a usual planar magnetron form, a representation of which is given in Figure 3A. A cross-sectional view of the magnet structure 55 is provided at a vertical plane. In plan view, the structure of Figure 3 is elongated in a direction normal to the plane of paper.

The structure of Figure 3A is termed a balanced magnetron. Its magnetic lines of force 131 all travel between one of the outer south magnetic poles and a central north pole. As is well known, electrons and ions travel in a spiral around a magnetic force line and along it, under influence of a combination of the magnetic field forces and the electric field forces formed by the cathode and the process chamber metal case. The cathode 57 is generally made of titanium or quartz, but sputtering is prevented from happening because of the higher pressure (that is, greater than the 1 to 5 microns of sputtering) used in the deposition system of Figure 2.

An unbalanced magnetron that alternatively can be utilized in the system of Figure 2 is shown in Figure 4A. Outside magnets 133 and 135 are arranged with a soft iron core 137 middle. Only the south magnetic poles are positioned against a cathode 57', the north pole faces being oriented away from the cathode. The result is that a substantial proportion of the magnetic field line follow a much longer path in extending between the magnetic south and north pole regions.

Only a small proportion of the force lines extend directly between the outer south pole faces and the central iron core piece. The result is a pattern of magnetic field lines, such as lines 139 of Figure 4A, which are directed towards the substrate 13, most of them substantially perpendicular to its surface. The result is a beneficial bombardment by ions and electrons in the plasma against the surface of the substrate 13. This is known to improve some properties of the resulting deposited film, such as its hardness. Also, the deposition rate has been found to be much better with an unbalanced magnetron structure of Figure 4A rather than the balanced magnetron structure of Figure 3A.

The balanced and unbalanced magnetrons have their relative magnetic field strength distribution across the cathode indicated by diagrams of Figures 3B and 4B, respectively. As can be seen in Figure 3B, the magnetic field strength in the center is twice the field strength of the outer poles. In the unbalanced magnetron case of Figure 4B, however, the center field strength is very weak compared to the field strength of each of the outer magnetic poles. This difference in field strength distribution across the cathode results in the different distribution of the magnetic flux lines 139.

The magnetron structures of Figures 3A and 4A are suitable for low frequency operation of the power supply 17. An example frequency is 40 kHz. However, there can be some advantages from operating at a much higher frequency, such as in the radio frequency range of several megahertz. Such a high frequency system is schematically illustrated in Figure 5. A magnetron magnetic assembly 55" is in this case made of a non-conductive quartz material. A radio frequency generator 141 has its output coupled to the cathode 57" by a rod 143. An impedance matching network 145 is connected between the RF generator and the coupling rod 143 in order to minimize any reflections from impedance discontinuities at the cathode 57".

The exemplified deposition chamber 29 had a size of 12 inches by 12 inches by 24 inches, and the vaporizing apparatus 71 is believed to have a maximum flow rate of about 700 SCCM for this dimensional scale which should be adequate for most applications. However, the vaporizing apparatus 71 is not limited to the exemplified dimensions since it can be readily scaled up.

### Experimental

All depositions were conducted by the general procedure now described and with an Airco Solar Products ILS-1600 research coater. The chamber was evacuated to a base pressure of not greater than about  $3 \times 10^{-6}$  Torr. The load lock was vented to atmosphere while the chamber was maintained under high vacuum. Then the load lock was evacuated with the substrate loaded therein. Meanwhile, the vaporizer had been heated to a constant temperature of 100°C, had vaporized organosilicon therein, but was isolated from the chamber until the gas inlet was opened. The vaporizing apparatus 71 was set for the desired flow reading of organosilicon. The desired gas flows of the additional components were set on each component's flow controller, and the pressure in the chamber was adjusted to the desired value by adjusting a baffle over the diffusion pump. The load lock-diffusion pump was closed and the valve isolating the load lock and the chamber was opened. After the pressure in the chamber stabilized, the power supply was turned on and adjusted to the desired value. Thus, the glow discharge plasma is established in the chamber. The pressure was again stabilized and adjusted if necessary. The desired process conditions were selected (power, current and voltage of the power

supply, the pressure of the chamber, the organosilicon flow, and the vaporizer pressure). An emission spectrum from the control program was used to find the appropriate hydrogen (alpha) to inert gas ratio. The organosilicon flow into the chamber was adjusted until the desired hydrogen (alpha) to inert gas ratio was obtained. The substrate was then conveyed back and forth through the plasma region until the desired coating thickness was achieved while continuing to monitor the process conditions and making appropriate adjustments according to the diagnostic method. Once the desired film thickness was obtained, the system was shut down and the coating substrate removed.

The following abbreviations will be used:

HMDSO - hexamethyldisiloxane

TMDSO - 1,1,3,3-tetramethyldisiloxane

MTMOS - Methyltrimethoxysilane

VTMS - Vinyltrimethylsilane

VTMEOS - Vinyltrimethoxysilane

SCCM - Standard Cubic Centimeters per Minute

IPM - Inches Per Minute

Te - Average electron temperature in electron volts

H - Hydrogen alpha emission line at 657 nm

%T - Percent transmission of light

%Rf - Percent reflection of coated side of sample

A%Rg - Percent reflectance of plain glass side of sample

A haze measurement represents the percent change in haze as a result of abrading the films with an abrasive wheel (CS-10F) with a 500 g load on a Taber abrader. The hardness values (or scratch resistance) were determined by ASTM D3363-74, where 0 means the least scratch resistance and 10 means no damage to the coating when scratched.

Aspects of the inventive process are now illustrated by the following examples. All were films produced on clear glass substrates.

#### Example 1

Four different gas streams were used to deposit thin films on glass substrates. The power was 1,000 watts, 40 kHz. The substrate conveyor speed was 10 IPM for all four, and each substrate was passed through the plasma five times. Composition (4) was a gas stream in accordance with the invention. Table 1, below, sets out the four gas stream compositions and the scratch resistant ratings of film produced from each composition.

Table I

<u>Composition</u>	<u>Gas Stream (SCCM)</u>	<u>Hardness</u>
1	20 HMDSO	2
2	20 Ar	2
3	20 HMDSO	3
4	20 He	9
	20 HMDSO	
	7 O <sub>2</sub>	
	35 HMDSO	
	35 O <sub>2</sub>	
	46 He	

As can be seen from Table I, the inventive gas stream provided a film with a hardness over four times harder than gas streams including either only argon or only helium rather than both, and three times harder than a gas stream with only oxygen. The process parameters for gas stream Composition (4) of Table I were Te of 1.49 ev and H/He of 1.22. The chamber pressure varied between 38 and 46 microns for the four different gas streams, and was 46 microns for the inventive gas stream composition (4).

Example II

Five different gas streams in accordance with the invention were utilized to demonstrate use of the inventive method to select properties such as deposition rate, film dereflection and film hardness. The conveyor speed for all five was 10 ipm, and the power was 1,000 watts, 40 kHz. The chamber pressure during the depositing for all five was 46 microns. Table II sets out the five different compositions and the various film and process properties.

Table II

<u>Inventive Composition</u>	<u>Gas Stream (SCCM)</u>	<u>Hardness</u>	<u>Deposition Rate (A/min)</u>	<u>% Rf</u>
5	35 HMDSO 35 O <sub>2</sub> 47 He 2.1 C <sub>3</sub> H <sub>6</sub>	7+	233	7.47
6	35 HMDSO 35 O <sub>2</sub> 46 He 10 N <sub>2</sub>	9-	195	7.85
7	35 HMDSO 30 O <sub>2</sub> 46 He 5 N <sub>2</sub> O	7	220	7.61
8	35 HMDSO 35 O <sub>2</sub> 46 He 2.1 C <sub>3</sub> H <sub>6</sub> 6.0 N <sub>2</sub>	9+	226	7.42
9	36 HMDSO 30 O <sub>2</sub> 47 He 2.1 C <sub>3</sub> H <sub>6</sub> 9.8 N <sub>2</sub> O	7	203	6.73

As can be seen from the data of Table II, the gas stream composition (8) provided an extremely hard film, while the other four inventive gas streams gave films with good harness at acceptable deposition rates. The film from gas stream composition (8) was formed by 37 passes, the films from gas stream compositions (5), (6) and (7) from seven passes, and that of gas stream composition (9) from five passes. Since uncoated glass has a %Rf of 7.86, the film from gas composition (9) was slightly dereflective on the coated side of the substrate. The %Rg on the plain glass side was similarly slightly reflective.

Example III

Four different inventive gas stream compositions were utilized with different organosilicons. The pressure during deposition in all four was 46 microns, the power was 1,000 watts, 40 kHz, the conveyor speed was 10 ipm, and there were five passes for each gas stream composition. The film hardnesses and two process parameters are set out in Table III.

Table III

	<u>Inventive Composition</u>	<u>Gas Stream (SCCM)</u>	<u>Hardness</u>	<u>Te</u>	<u>H /He</u>
5	10	39 TMDSO 45 O <sub>2</sub> 46 He	7	1.184	1.630
10	11	30 MIMOS 12 O <sub>2</sub> 90 He	7+	1.063	0.883
15	12	36 VIMS 35 O <sub>2</sub> 46 He	8	1.376	1.820
20	13	30 VIMEOS 30 He 16 O <sub>2</sub>	7+	0.430	0.960

As can be seen from the data in Table III, all four different organosilicons gave films of good hardness when processed in accordance with the invention. Inventive gas stream composition (10) had a deposition rate of 381 Angstroms per minute and an oxygen transmission rate of 0.0836 cc/100 in <sup>2</sup>/day at a 21% oxygen atmosphere. Thus, inventive gas stream composition (10) is particularly useful for rapidly coating substrates with a film which is substantially impermeable to oxygen. Additionally, gas stream composition (12) had only a 1.01% increase in "haze" after having been subjected to 100 revolutions of the Taber abrader. This excellent "haze" value is comparable to that of clear glass, and means the coating is especially suitable for applications where abrasive resistance is needed.

Example IV

Two identical gas stream compositions in accordance with the invention were prepared and processed under identical conditions, except that a standard, planar magnetron was utilized for one deposition and the preferred unbalanced magnetron was used for the other. Power for both processes was 1,000 watts, 40 kHz, conveyor speed was 10 ipm with ten passes for each, pressure was 46 microns during the depositing, and the deposited films both had a hardness rating of 7. One difference between the two processes was that the preferred unbalanced magnetron had a deposition rate about 15% greater than that with the planar magnetron. The films produced by use of the unbalanced magnetron were also found to be harder when the "haze" value was determined. FTIR analysis showed a higher degree of crosslinking. Both gas stream compositions and their flow rates were as set forth in inventive composition (8) of Example II.

Example V

Three similar inventive gas streams were processed with different power and/or frequency conditions. The data is set out in Table IV.



Table IV

<u>Inventive Composition</u>	<u>Gas Stream (SCCM)</u>	<u>O<sub>2</sub> Trans- mission Rate</u>	<u>Pressure (Microns)</u>	<u>Power</u>	<u>Deposition Rate (Å/min)</u>	
14	35 HMDSO 35 O <sub>2</sub> 46 He	0.259	46	1000 W, 40 kHz	217	5
15	35 HMDSO 35 O <sub>2</sub> 40 He	0.0469	46	375 W, 13.56 MHz	380	10
16	25 HMDSO 25 O <sub>2</sub> 33.2 He	1.05	15	300 W, D.C.	627	15

The film hardnesses of gas stream compositions (14) and (15) were both 7, and that of gas stream composition (16) was 6-. Thus, it can be seen the radio frequency processing of gas stream (15) provided an excellent non-permeable property at a very good deposition rate. The deposition rate for gas stream composition (16) was outstanding, but the film had a decreased light transmission (%T of 87), increased reflectances when compared with uncoated glass. Both gas stream compositions (14) and (15) provided films having light transmission similar to uncoated glass.

Example VI

The effect of pressure on the inventive process was studied with one composition maintained at either 97, 45 or 26 microns. The deposition rates for this composition, but at three different pressures, are set forth in Table V.

Table V

<u>Inventive Composition</u>	<u>Gas Stream (SCCM)</u>	<u>Pressure (Microns)</u>	<u>Deposition Rate</u>	
17	20 HMDSO 30 O <sub>2</sub> 40 He 1.2 C <sub>3</sub> H <sub>6</sub>	97	93	40
17	20 HMDSO 30 O <sub>2</sub> 40 He 1.2 C <sub>3</sub> H <sub>6</sub>	45	145	45
17	20 HMDSO 30 O <sub>2</sub> 40 He 1.2 C <sub>3</sub> H <sub>6</sub>	26	175	50

As may be seen from the data of Table V, the deposition rate improves as the pressure is reduced. The hardness value for film at 26 microns was 9+, while that of the film at 97 microns was 9. However, a preferred pressure range is from about 43 to about 49 microns because the FTIR revealed higher crosslinking.

Although the preceding examples illustrate films on clear, 1/8 inch thick glass, onto various plastics, onto

metals, and onto minerals such as crystalline silicon and KBr. Thus, the method is widely applicable.

While the invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modifications, and this application is intended to cover any variations, uses or adaptations of the invention following, in general, the principles of the invention and including such departures from the disclosure as come within the known or customary practice in the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth, and as fall within the scope of the invention and the limits of the appended claims.

## Claims

1. A method of depositing an adherent, silicon oxide based film comprising:

providing a gas stream including a volatilized organosilicon compound, oxygen, and an inert gas;

establishing a glow discharge plasma derived from the gas stream in a previously evacuated chamber, the chamber including a substrate removably positionable in the plasma; and

flowing the gas stream into the plasma to deposit a silicon oxide onto the substrate when positioned in the plasma, the deposited silicon oxide being a reaction product of the gas stream, the chamber being maintained at a pressure of less than about 100 microns during the depositing.

2. A method according to Claim 1, wherein the substrate is conveyed into and out of the plasma during the depositing.

3. A method of depositing a hard, substantially inorganic silicon oxide based film in a previously evacuated chamber by glow discharge comprising:

vaporizing an organosilicon component and admixing the volatilized organosilicon component with an oxygen component and an inert gas component to form a gas stream exterior the chamber;

establishing a glow discharge plasma in the chamber from one or more of the gas stream components;

controllably flowing the gas stream into the plasma while confining at least a portion of the plasma therein; and

conveying a substrate into and out of the plasma adjacent the confined plasma.

4. A method according to Claim 3, wherein the substrate is at a temperature below about 80°C during the conveying.

5. A method according to Claim 3 or Claim 4, wherein the substrate is electrically isolated from the chamber except for contact with the confined plasma.

6. A method according to any of Claims 3 to 5, further comprising magnetically confining at least a portion of the plasma adjacent to the substrate during the depositing to increase an ion flux thereat.

7. A method according to any one of the preceding Claims, wherein the chamber is maintained at a pressure of between about 20 to about 100 microns during the depositing.

8. A method of plasma enhanced thin film deposition comprising:

providing a gas stream including a volatilized organosilicon compound;

establishing a glow discharge plasma derived from the gas stream in a chamber previously evacuated to about  $10^{-6}$  Torr, the chamber including a substrate removably positioned in the plasma; and

flowing sufficient of the gas stream to establish a pressure in the chamber of about 25 to about 100 microns and depositing a silicon oxide film on the substrate when positioned in the plasma while magnetically confining at least a portion of the plasma adjacent the substrate during the depositing to increase an ion flux thereat.

9. A method according to any preceding Claim, wherein the organosilicon compound being flowed into the plasma is in an adjustably controlled amount.

10. A method according to Claim 9, wherein the organosilicon compound and oxygen of the gas stream being flowed into the plasma are in a flow rate ratio between about 1.2:1 to about 1:1.8 and the inert gas of the gas stream being flowed into the plasma is helium or argon in an amount effective to increase the deposition rate and the hardness of the deposited silicon oxide.

11. A method according to any preceding Claim, wherein the inert gas is helium and the gas stream being flowed into the plasma comprises organosilicon compound and oxygen in a ratio in the range from about 1.2:1 to about 1:1.8 and organosilicon compound and helium in a ratio in the range from about 1:1.5 to

1:2.3.

12. A method according to any preceding claim, wherein the organosilicon compound is 1,1,3,3-tetramethyldisiloxane, hexamethyldisiloxane, vinyltrimethylsilane, methyltrimethoxysilane, vinyltrimethoxysilane or hexamethyldisilazane.

13. A method according to any preceding Claim, wherein the deposited silicon oxide is substantially inorganic.

14. A method according to any one of Claims 1 to 12, wherein the inert gas is helium, the gas stream includes a minor amount of propylene, and the deposited silicon oxide includes carbon moieties.

15. A method according to any preceding Claim, wherein the gas stream includes a minor amount of nitrogen or nitrous oxide and the deposited silicon oxide includes nitrogen moieties.

16. A method of depositing a thin film on a substrate by a plasma process within an evacuated chamber, comprising the steps of:

providing a said chamber a gas stream that includes a source of a material desired to be deposited on said substrate,

establishing within said chamber a glow discharge plasma derived from the gas of said stream in a region of high electric field

removably positioning the substrate in said plasma without any electrical connection therewith,

generating within said plasma a magnetic field having a substantial magnetic flux directed against said substrate.

17. A method according to Claim 16, wherein the step of generating a magnetic flux includes positioning within said chamber two magnetic pole pairs, a first magnetic pole of each pair being oriented to face said plasma and a second magnetic pole of each pair being oriented to face away from said plasma.

18. A method according to Claim 16, wherein the step of generating a magnetic flux includes positioning within said chamber a magnetic structure having a surface adjacent said plasma that is characterized by a magnetic flux distribution function in substantially any direction thereacross which varies from a maximum magnetic strength of one polarity separated by a lesser magnetic strength of another polarity.

19. A method according to any of Claims 1 to 16, wherein the plasma is confined by means of an unbalanced magnetron.

20. The method according to Claim 19, wherein a vacuum pump is in fluid communication with the chamber, is spaced from the magnetron, and the gas stream is flowed into the plasma upstream or a vacuum pump used to evacuate the chamber and downstream of the magnetron.

21. A method according to any preceding Claim, wherein the substrate is glass, plastics, mineral or metal.

22. A method according to any preceding Claim, which comprises the step of evacuating the chamber to a pressure substantially within a range of about 43 to about 49 microns.

23. In a vacuum system wherein a thin film of material is deposited on a substrate positioned within a previously evacuated chamber glow discharge, comprising:

a vaporizer of sufficient construction for vaporizing a liquid having a boiling point above ambient temperature and delivering a controlled flow of a vapor into a previously evacuated chamber;

electrical means for establishing a glow discharge plasma in the chamber from the vapor;

a substrate positioned within the chamber; and

magnetic means for generating a magnetic field within the plasma having a substantial magnetic flux directed against the substrate.

24. A vacuum system according to Claim 23, further comprising at least one additional source of gas adapted to introduce such at least one additional gas along with the vapor into the chamber as a gas stream, and the glow discharge plasma being formed from said gas stream.

25. A vacuum system according to Claim 23 or 24, wherein the magnetic means includes an unbalanced magnetron positioned within the chamber.

26. A vacuum system according to Claim 24 or 25, wherein the magnetic means includes two magnetic pole pairs positioned within the chamber, a first magnetic pole of each pair being oriented to face the plasma and a second magnetic pole of each pair being oriented to face away from the plasma.

27. A vacuum system according to Claim 24 or 25, wherein the magnetic means comprises a magnetic structure positioned within the chamber having a surface adjacent the plasma that is characterized by a magnetic flux distribution function in substantially any direction thereacross which varies from a maximum magnetic strength of one polarity separated by a lesser magnetic strength of another polarity.

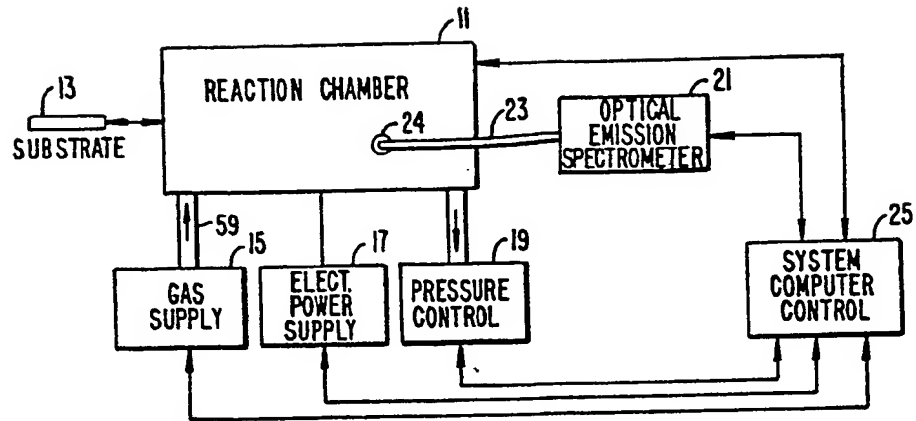


FIG. 1.

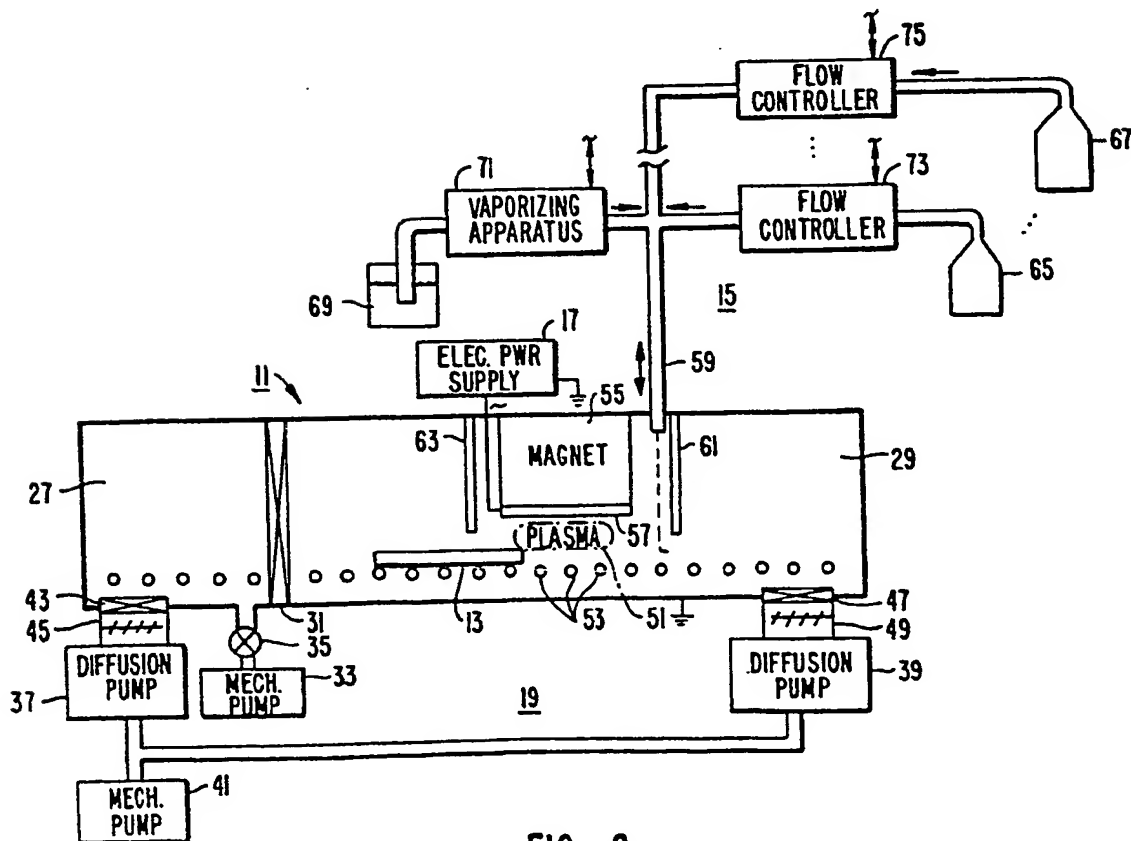


FIG. 2.

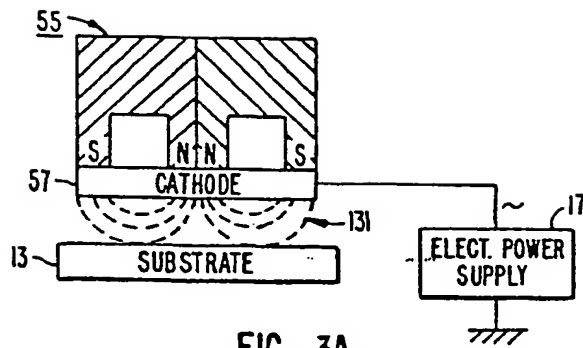


FIG. 3A.

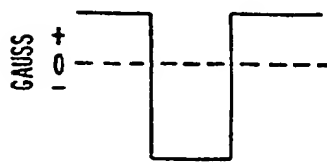


FIG. 3B.

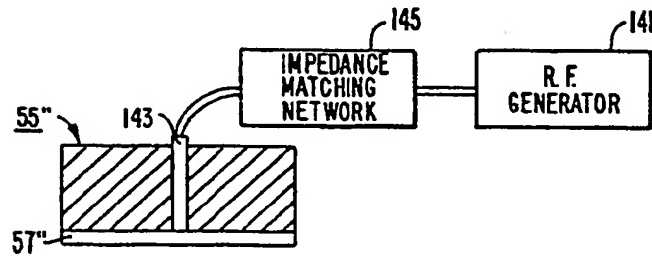


FIG. 5.

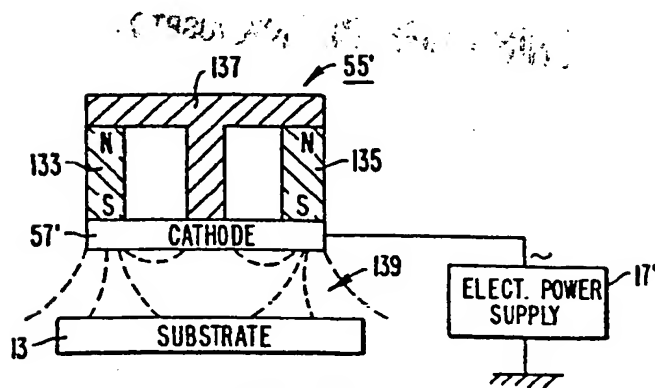


FIG. 4A.



FIG. 4B.

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(54) Method of plasma enhanced silicon oxide deposition.

(57) A method of depositing a hard silicon oxide based film is provided by controllably flowing a gas stream including an organosilicon compound into a plasma and depositing a silicon oxide onto a substrate while maintaining a pressure of less than about 100 microns during the depositing. The organosilicon compound is preferably combined with oxygen and helium and at least a portion of the plasma is preferably magnetically confined adjacent to a substrate during the depositing, most preferably by an unbalanced magnetron. These silicon oxide based films may be reproducibly deposited on small or large substrates, such as glass, plastic, mineral or metal, with preselected properties.

EP 0 299 754 A3



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# EUROPEAN SEARCH REPORT

Application number

EP 88306433.9

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	<u>US - A - 4 282 268</u> (PRIESTLEY) * Claims 1,2,6; example 1 *	1, 12, 13, 21	
A	<u>EP - A1 - 0 212 691</u> (FOCUS SEMICONDUCTOR) * Claims 1,5,6,9 *	1, 12, 13, 21	
A	<u>EP - A2 - 0 200 086</u> (ENERGY CONVERSION) * Page 12, lines 3-14; page 14, lines 7-17 *	1, 15, 21	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 23 C
Place of search VIENNA		Date of completion of the search 27-11-1990	Examiner WILFLINGER
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